

# Ni-Ti Alloys for Tribological Applications: The Role of In-Situ Nanotechnology

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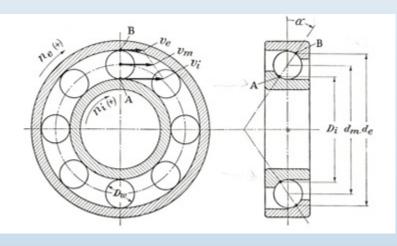


### Bearings 101: The what, where, whys and hows

- Definition: A bearing is a device that allows free movement between two connected machine parts.
  - Allows one part to turn while the other remains stationary (e.g. wheel vs. car frame, propeller vs. airplane wing).
  - Must operate with low friction and no wear.
  - Be able to withstand severe loads.
  - Ubiquitous (cars, planes, washing machines, spacecraft, pumps, fans, computer disk drives, roller skates and bicycles).
- Commonly rely on balls rolling between tracks (races).
- Bearing materials must be hard.









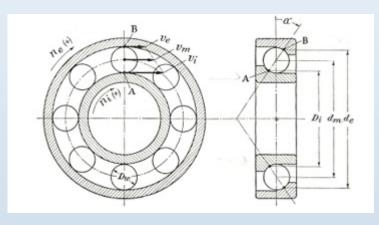
## Materials Requirements: NASA sets the bar high

(Space challenges conventional technology)

#### Attributes sought:

- Hard (Rockwell C58 or better)
- Wear-resistant and compatible with existing lubricants
- Resistant to rolling contact fatigue (RCF)
- Fracture resistant
- Corrosion resistant (preferably immune)
- Low density (to reduce centrifugal loads at high rpm)
- Capable of producing ultra-smooth surface finishes
- Dimensionally stable and easy to manufacture







## **Bearing Material: State-of-the-Art (SOA)**

(Current suite of candidates is severely limited)

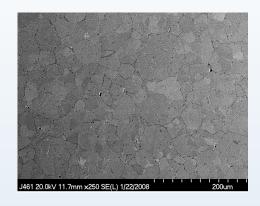
- Four general types of bearing materials:
  - Steels (Corrosion resistant steels, martensitic, austenitic)
  - Ceramics (Si<sub>3</sub>N<sub>4</sub> balls + steel races, a.k.a., hybrid bearings)
  - Superalloys (e.g., jet turbine blade alloys)
  - Non-ferrous alloys (bronze, nylon etc.)
- Each of these has inherent shortcomings:
  - Hard steels are prone to rusting (even "stainless steels" like 440C)
  - Superalloys and austenitic stainless steels (304ss) are soft.
  - Ceramics have thermal expansion mismatch and dent steel races
  - Non-Ferrous materials are weak and lack temperature capabilities
- No known bearing material blends all the desired attributes:
  - High hardness, corrosion immunity, toughness, surface finish, electrical conductivity, non-magnetic, manufacturability, etc.



### New approach: 60NiTi-Superelastic

(Hard but resilient material based upon shape memory alloys)

- 60NiTi Basics: market name NiTiNOL 60
  - Invented by W.J. Buehler (late 1950's) at the Naval Ordnance Laboratory (NiTiNOL stands for Nickel-Titanium Naval Ordnance Lab).
  - Contains 60 wt% Nickel and 40 wt% Titanium
  - 60NiTi is not a metal or a ceramic: a weakly ordered inter-metallic compound.
  - A close cousin to the shape memory alloy, NiTiNOL 55, but 60NiTi is dimensionally stable.
  - 60NiTi is bearing hard (Rockwell C60) but only half as stiff as steel.
  - Buehler found 60NiTi too difficult to manufacture but modern (ceramic) processing methods enable 60NiTi bearings with remarkable properties.



60NiTi microstructure



Highly polished 60NiTi bearing balls



#### **Nitinol 60: Material Peculiarities**

#### Puzzling Mechanical Behavior:

- Measured elastic (stress-strain) properties exhibits nearly 10X more deflection than steel.
- Conventional wisdom: hard and stiff go together yet despite its high hardness, 60NiTi is highly elastic (not so stiff).

#### Question:

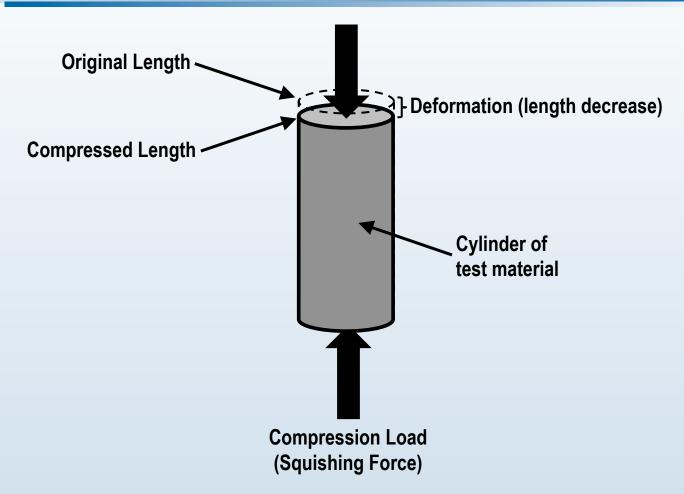
– What are the reasons behind NiTi's high hardness yet modest elastic stiffness?

#### Longer term potential:

- Could the unique combination (hard yet superelastic) yield new benefits?
- Could the NiTi materials system be the basis for new applications?



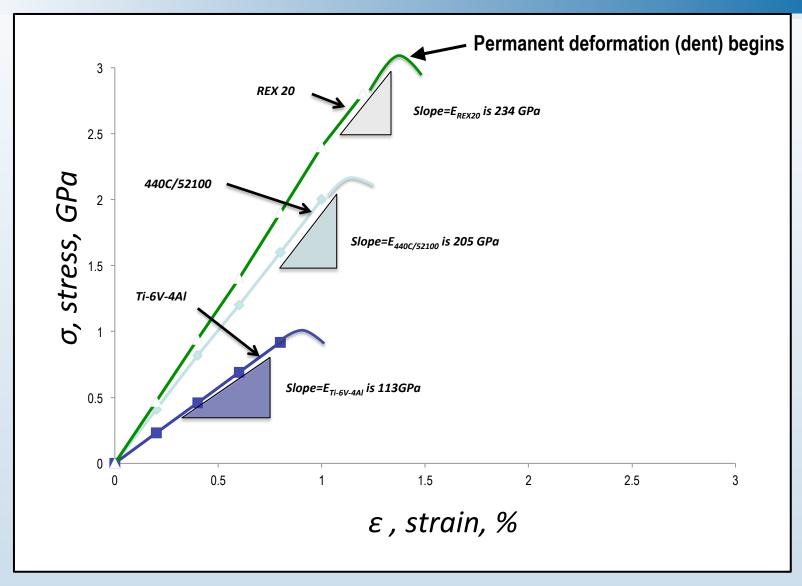
# **Conventional Metals: Elastic Behavior**



- •Deformation is proportional to the elastic modulus (stiffness), not hardness.
- •Length is regained when load is removed (elastic) just like a spring.
- •If load exceeds yield (plastic) permanent length reduction (dent) occurs.

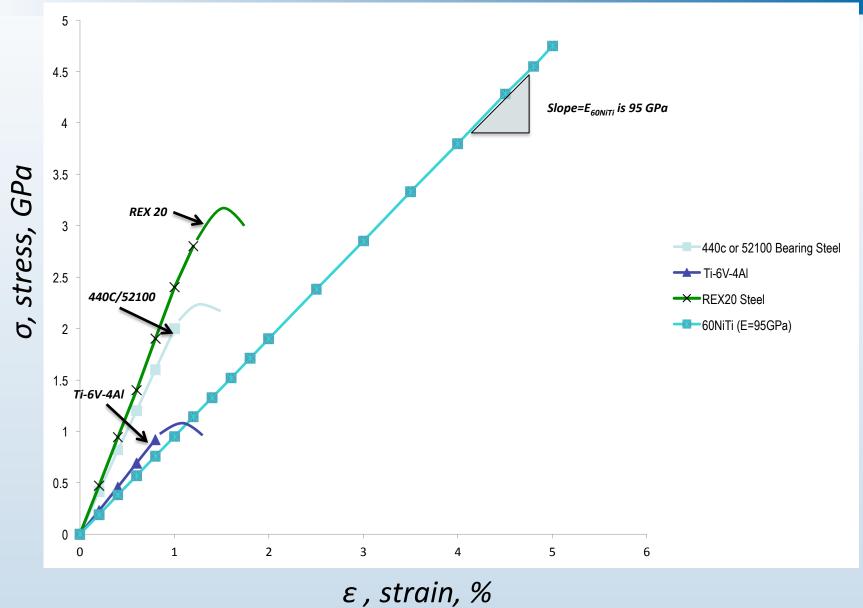


# **Conventional Metals: Elastic Behavior**





## 60NiTi: Stress-Strain Behavior





## **Technical Properties Comparison:**

_				
Property	60NiTi	440C	$\mathrm{Si}_{3}\mathrm{N}_{4}$	M-50
Density	6.7 g/cc	7.7 g/cc	3.2 g/cc	8.0 g/cc
Hardness	56 to 62 HRC	58 to 62 HRC	1300 to 1500 Hv	60 to 65 HRC
Thermal conductivity W/m-°K	~9 to 14	24	33	~36
Thermal expansion	~11.2×10 <sup>-6</sup> /°C	10×10 <sup>-6</sup> /°C	2.6×10 <sup>-6</sup> /°C	~11×10 <sup>-6</sup> /°C
Magnetic	Non	Magnetic	Non	Magnetic
Corrosion resistance	Excellent (Aqueous and acidic)	Marginal	Excellent	Poor
Tensile/(Flexural strength)	~1000(1500) MPa	1900 MPa	(600 to 1200) MPa	2500 MPa
Young's Modulus	~95 GPa	200 GPa	310 GPa	210 GPa
Poisson's ratio	~0.34	0.3	0.27	0.30
Fracture toughness	~20 MPa/√m	22 MPa/√m	5 to 7 MPa/√m	20 to 23 MPa/√m
Maximum use temp	~400 °C	~400 °C	~1100 °C	~400 °C
Electrical resistivity	~1.04×10 <sup>-6</sup> Ω-m	~0.60×10 <sup>-6</sup> Ω-m	Insulator	~0.18×10 <sup>−6</sup> Ω-m

#### Primary Points

- Modulus is  $\frac{1}{2}$  that of steel, yet hardness is comparable.
- Tensile strength akin to ceramics.



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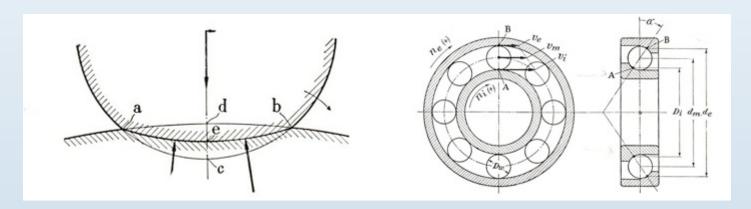
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# Low Modulus + Hard: A Technical Opportunity

- Surprising and relevant behavior:
  - It is contrary to a century of experience with hard bearing materials!
  - Hard bearing materials are stiff and unforgiving and yield after small deformations.
  - Small contact points result in high stress and damage even under modest loads.
  - Brinell denting test can quantify resilience effect.



Balls touch races at small points causing race surface dents

Dents on race surface cause rough running and premature failure



## Resilience: Can 60NiTi withstand high dent loads?

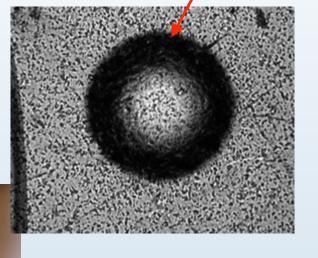
(Static denting behavior)

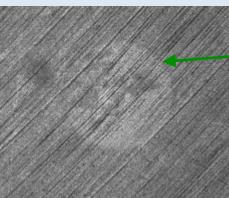
60NiTi dent resistance

Threshold load to damage

Critical to launch vehicles and aircraft

Deep Brinell dent.



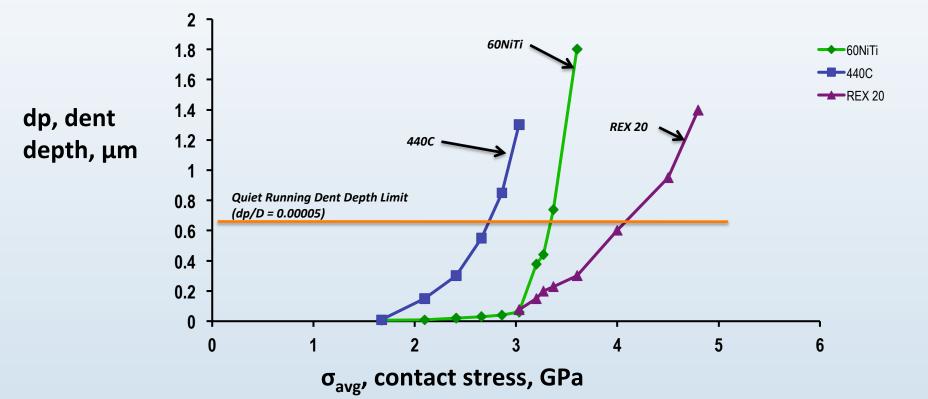


Threshold load visible dent.



## **Dent Depth vs. Hertz Contact Stress**

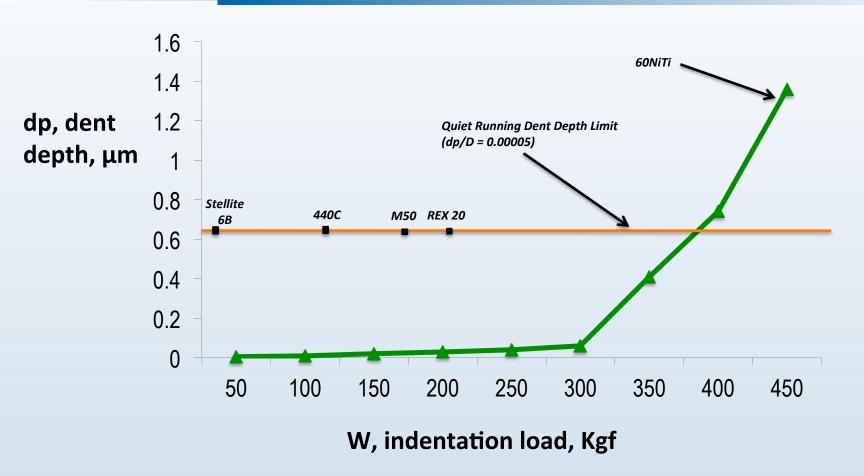
(12.7 mm diameter Si<sub>3</sub>N<sub>4</sub> ball against 60NiTi plate)





## **Dent Depth vs. Load**

(Si<sub>3</sub>N<sub>4</sub> ceramic ball pressed against 60NiTi plate)



60NiTi combines high hardness, reduced stiffness and superelasticity to increase load capacity over other steels dramatically. Immunity to rust is an added bonus!

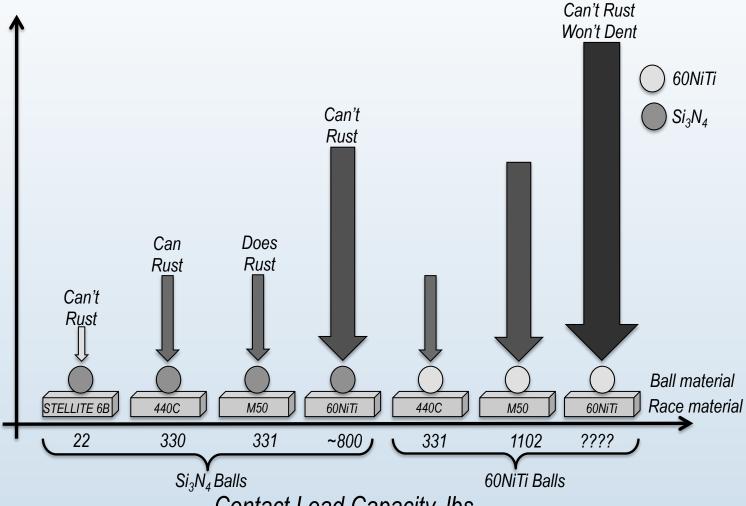


## Damage Threshold Load Capacity: Comparison

(1/2" Diameter ball pressed into plate)



Indent test



Contact Load Capacity, Ibs.

Low modulus + high hardness +superelasticity = extreme load capacity



#### **Nitinol 60: Material Peculiarities**

#### Puzzling Mechanical Behavior:

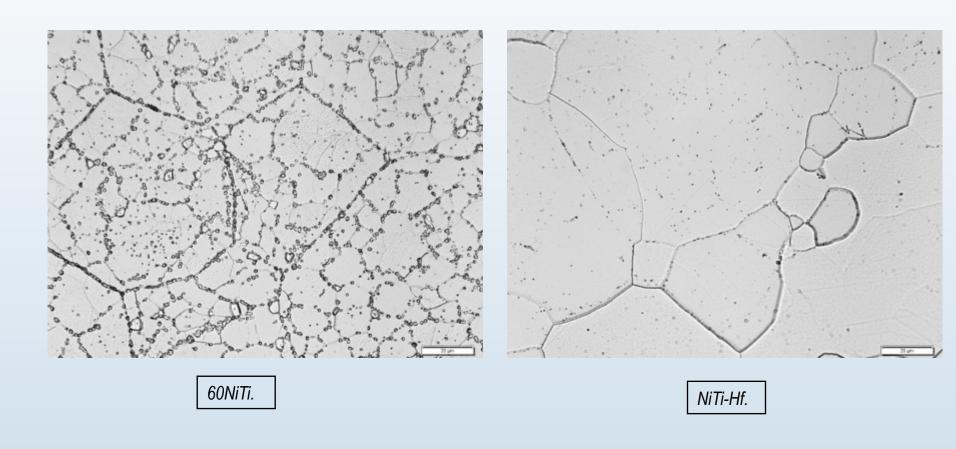
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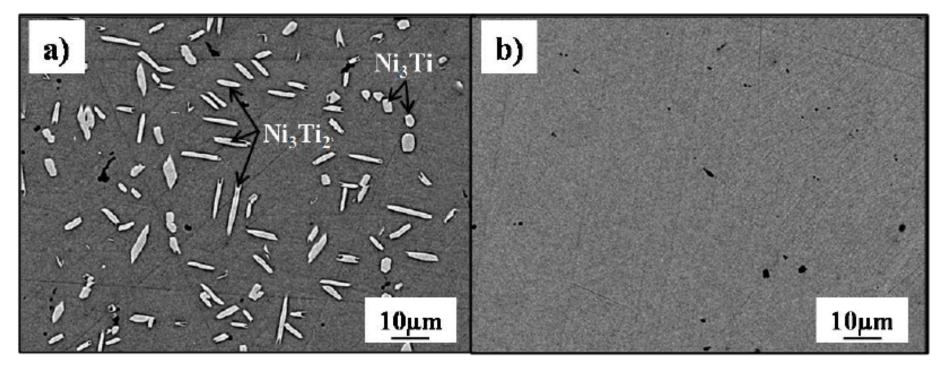
# Nitinol 60: Microstructures-Optical View



Standard Heat treatment#1: 1000C + Water Quench



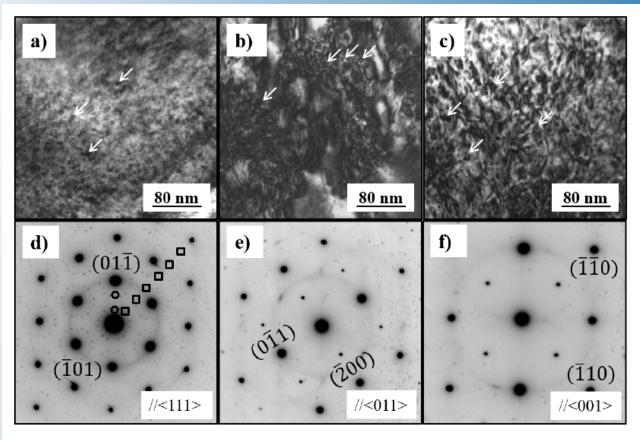
### Nitinol 60: Microstructures-SEM View



**Figure 3:(a)** BSE SEM micrograph of the 57NiTi solutionized/quenched microstructure revealing coarse Ni<sub>3</sub>Ti and Ni<sub>3</sub>Ti<sub>2</sub> precipitates, indicated by the arrows, in a B2 matrix. **(b)** BSE SEM micrograph of the 54NiTi solutionized/quenched microstructure where no obvious coarse precipitates were observed at this magnification. The fine scale of the Ni<sub>4</sub>Ti<sub>3</sub> precipitates in both alloys precluded their observation by SEM at this magnification.



#### Nitinol 60: Microstructures-TEM View

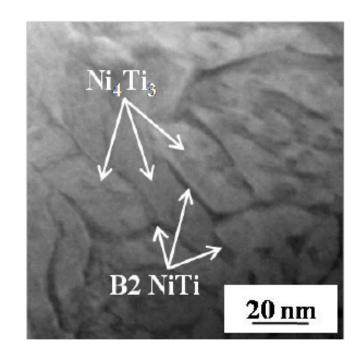


**Figure 4**: Multiple beam bright field image of the solution annealed condition for **(a)** 53NiTi, **(b)** 56NiTi, and **(c)** 58NiTi. Note the stark difference in strain contrast as Ni content is increased especially from 53NiTi to 56Ni. SAED patterns for the solution annealed condition for the 54NiTi sample from **(d)** the [111] zone axis of B2 matrix phase with squares highlighting the Ni<sub>4</sub>Ti<sub>3</sub> reflections and circles highlighting the R-phase, **(e)** the [011] zone axis of B2 matrix phase, and **(f)** the [001] zone axis of B2 matrix phase.

Conventional TEM Hints at a hardening phase but cannot see it



## Nitinol 60: Super-TEM View



**Figure 5**: STEM-HAADF image from a 55NiTi alloy to give prospective of Ni<sub>4</sub>Ti<sub>3</sub> spacing and narrow B2 NiTi channels between the precipitates. Ni<sub>4</sub>Ti<sub>3</sub> volume fraction was ~ 69%.

## NiTi-Hf Alloy: STEM reveals same nanophase

B.C. Hornbuckle et al./Journal of Alloys and Compounds 640 (2015) 449-454

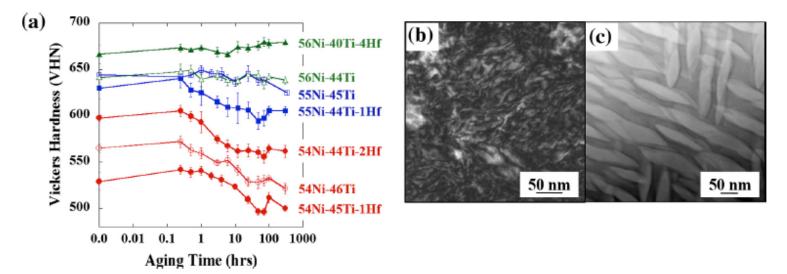


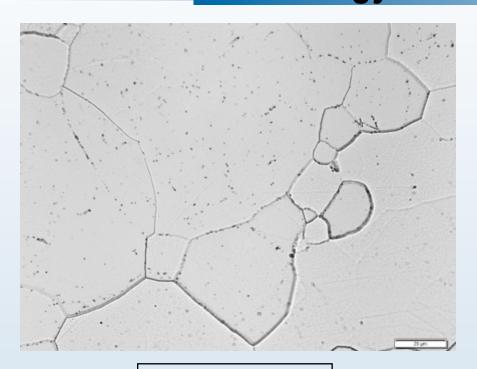
Fig. 1. (a) 400 °C aging curves for various Ni-rich binary and temary Ni-Ti alloys; note the binary data is from [8]. (b) Bright-field image and (c) STEM-HAADF image of the 54Ni-44Ti-2Hf solutionized/quenched microstructure. Note the significant strain contrast generated from the high volume fraction of Ni<sub>4</sub>Ti<sub>3</sub> precipitates in (b) and the nanoscale Ni<sub>4</sub>Ti<sub>3</sub> precipitates and narrow B2 matrix channels revealed in (c).

STEM HAADF-NiTi-Hf alloy also shows Ni4Ti3 Phase-refined.

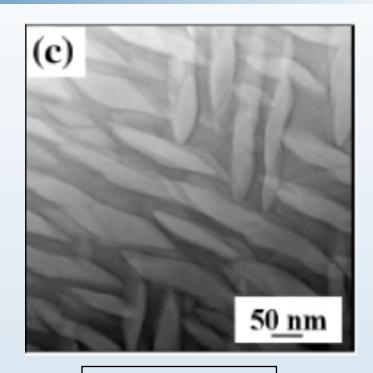
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# NiTi Alloys: Hardened by naturally formed nanotechnology



NiTi-Hf. (~500x, optical microscope)



NiTi-Hf. (~50,000x, STEM microscope)

#### Takeaway Points

- In-situ formation of hard nano-scale Ni4Ti3 particles hardens alloy.
- Revealed by exotic and recent microscopy technology.
- Knowledge aids and guides future development.



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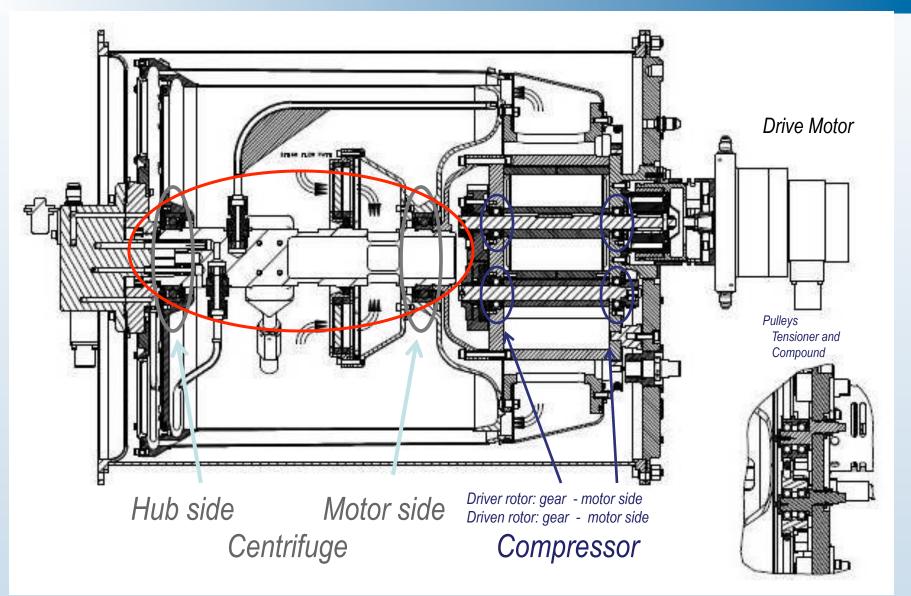
# Dent and Corrosion Resistant Ball Bearings



Finished 60NiTi-Hybrid Bearing



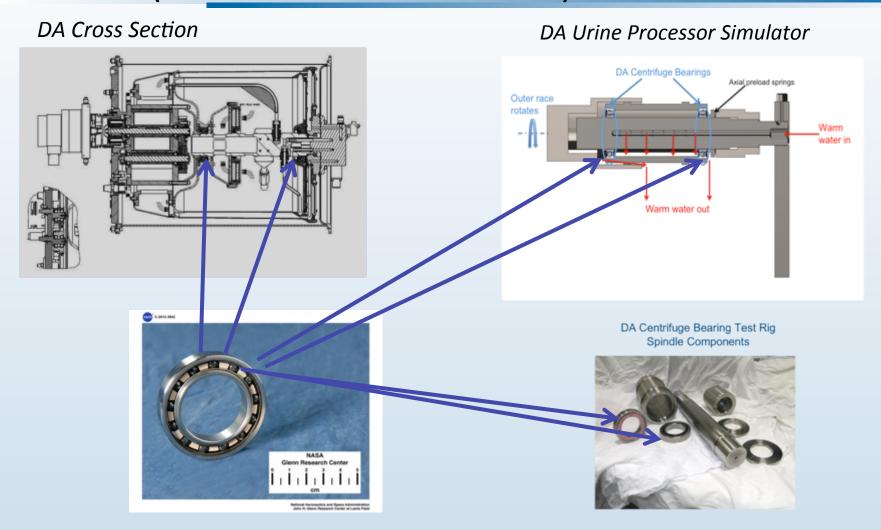
# ISS DA Centrifuge Bearings: 60NiTi Application





# **Bearing Testing:**

(Warm, wet, slow conditions)



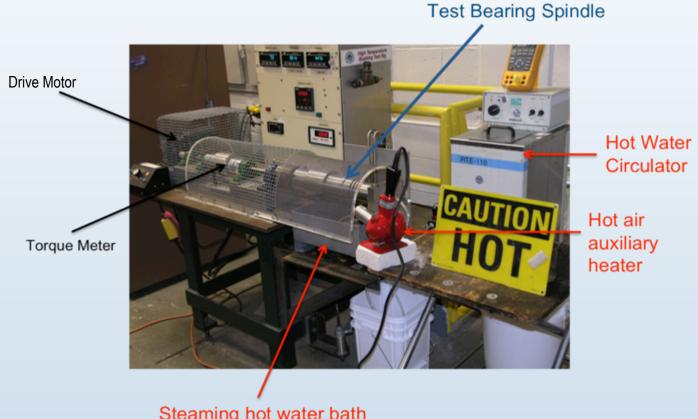
Speed, load, configuration, temperature and moisture match ISS application.



## **Bearing Testing:**

(Warm, wet, slow conditions)

#### Lab Configuration of DA Urine Processor



Steaming hot water bath

Over 10,000 operating hours has been demonstrated.



## DA Bearing: 60NiTi-Hybrid (50mm)

Post-Test Steel vs. 60NiTi-Hybrid

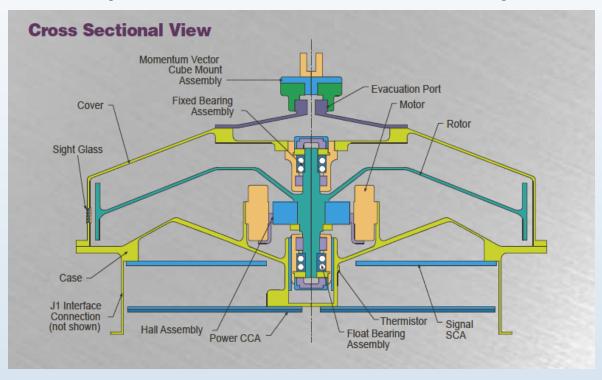


Test Results: 60NiTi bearings turn but don't rust!



## **Space Bearing Application: Game Changer**

#### **Typical Reaction Wheel Assembly**



- -60NiTi bearing races offer 2x (vs. Rex20) to 5x (440C) improvement.
- -Adoption of NiTi bearings enables the elimination of half the ball bearings, reducing friction by half with considerable cost and weight savings.

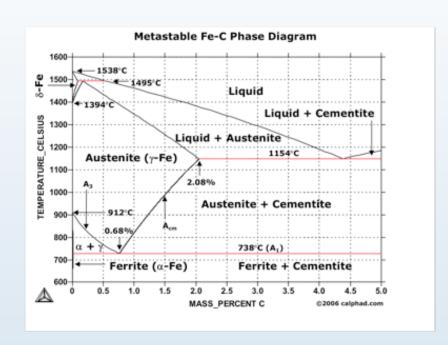


## Summary: NiTi is a new nanotechnology!

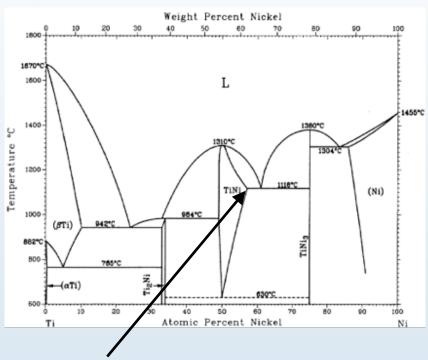
- NiTi alloy R&D initially followed conventional macro and microscopic maturation path.
- Macro-level properties hinted at something unusual driving behavior at microscopic level.
- Traditional microscopic level tools were unsuccessful in deciphering the mechanisms responsible for behavior (and revealing clues to further improvements).
- High resolution-nontraditional microscopy revealed in-situ formed nanoscale phase drives macroscopic properties.
- With this knowledge we are now positioned to push the technology forward.



## **Future View: Materials Design Space**



Fe-C system has yielded literally thousands of alloys and variants following centuries of development.



NiTi explorations to date have been limited to a very narrow region.

Though much more R&D remains to commercialize 60NiTi and other superelastic intermetallic materials for use in bearings, gears and other mechanical systems, early indications are very promising.



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